

FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE
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 CONCERNING A FILING UNDER 35 U.S.C. 371

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09/890348

INTERNATIONAL APPLICATION NO.:
 PCT/FR00/00205

INTERNATIONAL FILING DATE:
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PRIORITY DATE CLAIMED:
 29 JANUARY 1999

TITLE OF INVENTION: METHOD FOR PRODUCING CELLULOSE SULFOACETATE DERIVATIVES AND PRODUCTS AND MIXTURES THEREOF

APPLICANT(S) FOR DO/EO/US: Gaëlle CHAUVELON, Luc SAULNIER, Alain BULEON, and Jean-François THIBAUT

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. (see attached copy of PCT/IB/308)
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Item 11. to 16. below concern document(s) or information included:
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☐ A **FIRST** preliminary amendment.
 14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 15. ☐ A substitute specification.
 16. ☐ A change of power of attorney and/or address letter.
 16. ☐ Other items or information:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT PCT/IPEA/409 & ANNEXES
 INTERNATIONAL SEARCH REPORT (PCT/ISA/210)
 Forms PCT/IB/304 and PCT/IB/308
 Application Data Sheet and an ABSTRACT of the disclosure on a separate sheet

U.S. APPLICATION NO. (If known, give 37 CFR 1.13) **09/890348**INTERNATIONAL APPLICATION NO.
PCT/FR00/00205ATTORNEY'S DOCKET NO.
001K US 380817. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$ 1,000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$ 860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$ 710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$ 100.00

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Surcharge of \$130.00 for furnishing the oath or declaration later than 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	20 - 20 =	0	X \$18.00	\$
Independent claims	1 - 3 =	0	X \$80.00	\$
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			+ \$270.00	\$

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SUBTOTAL =

Processing fee of \$130 for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.49(f)).

TOTAL NATIONAL FEE =

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

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- a. ☒ A check in the amount of \$ 1,120.00 to cover the above fees is enclosed.
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July 30, 2001

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APPLICATION INFORMATION

Title Line One:: METHOD FOR PRODUCING CELLULOSE
Title Line Two:: SULFOACETATE DERIVATIVES AND PRODUCTS
Title Line Three:: AND MIXTURES THEREOF
Total Drawing Sheets:: 1
Formal Drawings?:: YES
Application Type:: UTILITY
Docket Number:: 001K US 3808

REPRESENTATIVE INFORMATION

Representative Customer Number:: 000466

CONTINUITY INFORMATION

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>Application One:: PCT/FR00/00205
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PRIOR FOREIGN APPLICATION

Foreign Application One:: 99/01049
Filing Date:: 29 JANUARY 1999
Country:: FRANCE
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PATENT
Atty. Docket No. 001K US 3808

IN THE U.S. PATENT AND TRADEMARK OFFICE

In re application of: Gaëlle CHAUVELON et al.

Appl. No.: 09/890,348
(PCTFR00/00205)

Group:

Filed: July 30, 2001 Examiner:

For: METHOD FOR PRODUCING CELLULOSE
SULFOACETATE DERIVATIVES AND PRODUCTS AND
MIXTURES THEREOF

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to the first Official Action and calculation of the filing fee, the following preliminary amendments and remarks are respectfully submitted in connection with the above-identified application.

IN THE SPECIFICATION:

Please add the following three new paragraphs before the paragraph beginning on page 9, between lines 26 and 27:

--As Fig. 1 shows, the acetic anhydride quantity added to a cellulose residue should be lower than about 2 to 7 mols per mol of anhydroglucose and, preferably, about 3.2 mols per mol of anhydroglucose. Lower acetic anhydride quantities do not allow any esterification in the conditions indicated in Fig. 1 (time:

30 minutes, temperature: 40°C) and higher quantities lead to the formation of a cellulose triacetate.

Fig. 2 shows that the reaction time should be below 1 hour and preferably of about 20 to 30 minutes in the conditions indicated in Fig. 2 (temperature and reactive quantity). For a reaction time superior or equal to about 1 hour, the esterification produces cellulose triacetate.

Both figures illustrate the production of an esterification residue which is rich in non cellulose polymers. This residue is not obtained for high purity celluloses.--

IN THE CLAIMS:

Please substitute claims 1-20 as originally filed, which appear on pages 14-16, with claims 1-22 as filed in the Article 34 amendment of January 23, 2001. The pages containing claims 1-22 are marked "AMENDED SHEET" and are attached hereto. Following the insertion of claims 1-22, please amend these claims as follows:

Please amend claim 5 as follows:

--5. (Amended) Process according to claim 3, characterized in that, at the step (vii), the blend is put at a temperature of about 4°C for about 16 hours.--

Please amend claim 6 as follows:

--6. (Amended) Process according to claim 3, characterized in that the step (ix), is carried out by a slow addition of a sodium hydroxide solution until a pH of about 7.5 is reached.--

Please amend claim 7 as follows:

--7. (Amended) Process according to claim 3, characterized in that at the step (ix) the blend is cooled in an ice bath and the pH is continuously followed so that the pH does not exceed 10.--

Please amend claim 9 as follows:

--9. (Amended) Process according to claim 1, characterized in that the chosen acetic anhydride quantity is 3.2 mols/mol of anhydroglucose.--

Please amend claim 10 as follows:

--10. (Amended) Process according to claim 1, characterized in that the chosen esterification time ranges from 20 to 30 mn.--

Please amend claim 11 as follows:

--11. (Amended) Process according to claim 1, characterized in that the chosen esterification temperature is 40°C.--

Please amend claim 12 as follows:

--12. (Amended) Process according to claim 1, characterized in that the starting cellulose material is selected in the group comprising cellulose residues purified from co-products derived from agriculture and, more particularly, from cereal bran, for example wheat and corn, but also from wood cellulose, for example, pine-tree, or microcrystalline cellulose.--

Please amend claim 14 as follows:

--14. (Amended) Derivative blend according to claim 13, characterized in that said derivatives have a sulphation degree ranging from 0.2 to 0.6.--

Please amend claim 16 as follows:

--16. (Amended) Derivative blend according to claim 13, characterized in that only the carbon atom which is in position 6 of the anhydroglucose cycles of said derivatives is sulphated.--

Please amend claim 17 as follows:

--17. (Amended) Derivative blend according to claim 13, characterized in that said derivatives have a viscosimetric mean polymerization degree determined in cupric ethylene diamine at 25°C ranging from 210 to 1590.--

Please amend claim 18 as follows:

--18. (Amended) Derivative blend according to claim 15, characterized in that said blend intrinsic viscosity, determined by extrapolation at nil concentration of the reduced viscosity measured in water at 25°C ranges from 600 to 1500ml/g.--

Please amend claim 19 as follows:

--19. (Amended) Blend according to claim 13, characterized in that said derivatives have such water retention properties that in the presence of salts, they swell up to 200 ml/g while remaining insoluble.--

Please amend claim 20 as follows:

--20. (Amended) Blend according to claim 13, characterized in that it is free from triacetylated derivatives.--

Please amend claim 21 as follows:

--21. (Amended) Blend according to claim 13, characterized in that said derivatives are thermally stable for 16 hours at 80°C.--

Please amend claim 22 as follows:

--22. (Amended) Blend according to claim 13, characterized in that it has the form of a thermoreversible and partially thixotropic gel.--

REMARKS

Claims 5-7, 9-12, 14, and 16-22 have been amended to eliminate multiple dependencies.

The amendment to the specification, and the substitution of claims 1-22 merely place this national phase application in the same condition as it was during Chapter II of the International Phase.

Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly requested.

Should there be any matters that need to be resolved in the present application, the Examiner is respectfully requested to contact the undersigned at the telephone number listed below.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE."

The Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 25-0120 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17.

Respectfully submitted,

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Attachments

March 4, 2002

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

Three new paragraphs have been added on page 9, between lines 26 and 27.

IN THE CLAIMS:

The claims have been amended as follows:

--5. (Amended) Process according to claim 3 [or 4], characterized in that, at the step (vii), the blend is put at a temperature of about 4°C for about 16 hours.--

--6. (Amended) Process according to [anyone of claims 3 to 5] claim 3, characterized in that the step (ix), is carried out by a slow addition of a sodium hydroxide solution until a pH of about 7.5 is reached.--

--7. (Amended) Process according to [anyone of claims 3 to 6] claim 3, characterized in that at the step (ix) the blend is cooled in an ice bath and the pH is continuously followed so that the pH does not exceed 10.--

--9. (Amended) Process according to [anyone of the preceding claims] claim 1, characterized in that the chosen acetic

anhydride quantity is 3.2 mols/mol of anhydroglucose.--

--10. (Amended) Process according to [anyone of the preceding claims] claim 1, characterized in that the chosen esterification time ranges from 20 to 30 mn.--

--11. (Amended) Process according to [anyone of the preceding claims] claim 1, characterized in that the chosen esterification temperature is 40°C.--

--12. (Amended) Process according to [anyone of the preceding claims] claim 1, characterized in that the starting cellulose material is selected in the group comprising cellulose residues purified from co-products derived from agriculture and, more particularly, from cereal bran, for example wheat and corn, but also from wood cellulose, for example, pine-tree, or microcrystalline cellulose.--

--14. (Amended) Derivative blend according to [the preceding claim] claim 13, characterized in that said derivatives have a sulphation degree ranging from 0.2 to 0.6.--

--16. (Amended) Derivative blend according to [anyone of claims 13 to 15] claim 13, characterized in that only the carbon

atom which is in position 6 of the anhydroglucose cycles of said derivatives is sulphated.--

--17. (Amended) Derivative blend according to [anyone of claims 13 to 16] claim 13, characterized in that said derivatives have a viscosimetric mean polymerization degree determined in cupric ethylene diamine at 25°C ranging from 210 to 1590.--

--18. (Amended) Derivative blend according to [anyone of claims 15 to 17] claim 15, characterized in that said blend intrinsic viscosity, determined by extrapolation at nil concentration of the reduced viscosity measured in water at 25°C ranges from 600 to 1500ml/g.--

--19. (Amended) Blend according to [anyone of claims 13 to 18] claim 13, characterized in that said derivatives have such water retention properties that in the presence of salts, they swell up to 200 ml/g while remaining insoluble.--

--20. (Amended) Blend according to [anyone of claims 13 to 19] claim 13, characterized in that it is free from triacetylated derivatives.--

--21. (Amended) Blend according to [anyone of claims 13

to 20] claim 13, characterized in that said derivatives are thermally stable for 16 hours at 80°C.--

--22. (Amended) Blend according to [anyone of claims 13 to 21] claim 13, characterized in that it has the form of a thermoreversible and partially thixotropic gel.--

Method for producing cellulose sulfoacetate derivatives and products and mixtures thereof

The present invention relates to a process for directly obtaining
5 sulfoacetate derivatives as well as the sulfoacetate derivatives which may
be obtained with this process.

The cellulose acetates are the most commonly industrially manufactured cellulose derivatives.

Cellulose acetylation is not actually specific and generally only the
10 cellulose triacetates are directly obtained.

Thus, acetylation rate control is not possible in the course of the reaction, which does involve a major problem as it is generally admitted that the solubility and the properties of the resulting derivative are directly related to the cellulose acetylation degree (number of acetylated hydroxyl functions per anhydroglucose unit).

In most techniques according to the prior art, obtaining hydrosoluble cellulose acetate, usually having an acetylation degree within the range from 0.5 to 1, goes through the formation of a cellulose triacetate followed by an acetolyse deacetylation, for example, according to Tanghe L.J. et al. (1963) : "Cellulose acetate" in Methods in Carbohydrate Chemistry. Vol. 3, Whistler R.L. (éd.) 193-212, Academic Press, New York or according to Samios E. et al. (1997) : "Preparation, characterization and biodegradation studies on cellulose acetates with varying degrees of substitution", Polym., 38 (12) : 3045-3054. Said deacetylation may further be performed by methanolysis, for example, according to Buchanan C.M., (1991) : "Preparation and characterization of cellulose monoacetates : the relationship between structure and water solubility", Macromol., 24 : 3060-3064.

These prior methods involve a considerable extra cost — time, reactive consumption — which excludes contemplating a commercialisation of hydrosoluble cellulose acetates. Moreover, during the acetylation and deacetylation steps, a strong depolymerization of these derivatives occurs, which affects their rheological properties.

Indeed, according to Aikhodzhaev B.I., et al. (1982) : "Preparation
35 and study of the properties of primary soluble cellulose acetates with low

degree of substitution", it would be possible to prepare hydrosoluble cellulose acetate directly. But this teaching does not mention anything about the production of sulphated derivatives and the described operational conditions seem to lead to a strong depolymerization of cellulose due to the presence of sulphuric acid in a considerable quantity.

The present invention, as far it is concerned, aims at offering a process for directly producing hydrosoluble sulphated cellulose acetate derivatives in that it does not include a preliminary deacetylation step of cellulose triacetates and this, practically, with no depolymerization of the cellulose chain.

More particularly, the invention relates to a process for producing hydrosoluble sulphated cellulose acetate derivatives with a polymerization degree equal to at least 0.8 times that of the initial cellulose.

The present invention also relates to cellulose sulfoacetates adapted to be obtained through such a process and which have more particularly the following advantages and/or features :

- variable acetylation degrees, depending on the origin of the cellulose of the starting cellulose material,
- a sulphation degree ranging from 0.6 to 0.2 (depending on the reaction length), being approximately 0.3 in the generally used reaction conditions,
- a controlled polymerization degree,
- an excellent solubility in water and polar solvents, and advantageous rheological properties due to their high viscosity, similar to those of associative polymers,
- a water retention in the presence of salt : they swell up to 190 ml/g, but remain soluble.

The present invention will now be described more in detail as far as its objects and other features are concerned, and making use of examples given merely by way of illustration and not of limitation, referring to the accompanying drawing in which :

Fig. 1 shows a diagram illustrating an optimization example of the acetic anhydride quantity (in mols of acetic anhydride per mol of anhydroglucose) for an esterification time of 30 minutes, and

Fig. 2 shows a diagram illustrating an optimization example of the cellulose esterification time for an acetic anhydride quantity of 3.2 mols/mol of anhydroglucose.

The present invention more precisely aims at offering a process for
 5 directly producing a blend of hydrosoluble cellulose sulfoacetate derivatives through esterification of a cellulose material, characterized in that it involves the steps comprising :

- (i) suspending the cellulose material in a glacial acetic acid solution and eliminating the acetic acid excess,
- 10 (ii) suspending the cellulose material swollen with acetic acid in a sulphuric acid solution in the glacial acetic acid, and
- (iii) reacting the cellulose material by adding the acetic anhydride.

Preferably, the process according to the invention comprises a step
 15 (iv) during which the reaction in step (iii) is stopped by adding an aqueous solution of acetic acid.

According to a preferred embodiment, the process according to the invention comprises the steps of :

- (v) optionally centrifuging the blend of the above-mentioned step (iv),
- (vi) washing and eliminating the optionally obtained culot,
- 20 (vii) adding water in order to precipitate the optionally generated cellulose triacetates,
- (viii) centrifuging and eliminating the residue,
- (ix) neutralizing the supernatant by optionally cooling,
- (x) dialyzing the resulting precipitate, and
- 25 (xi) freeze-drying the solution.

In such an embodiment, advantageously at step (vi) the optionally obtained residue is washed three times with acetic acid, and then three times with deionized water.

It is also preferable to put, at step (vii), the blend at a temperature
 30 within the range from 4 to 25°C, preferably about 4°C, for a period of time ranging from 1 to 24 hours, preferably about 16 hours.

Still in this embodiment, it is preferred that the step (ix) be performed by a slow addition of a sodium hydroxide solution until a pH of about 7.5 is reached.

Similarly, advantageously this same step (ix) will also be carried out by cooling the blend in an ice bath and to follow the pH continuously so that the pH does not exceed 10, preferably about 7.5.

According to another also preferred embodiment, step (x) of the process according to the present invention may be replaced by several washings with ethanolic solutions advantageously made of 60 %, 70 %, 80 % and 100 % ethanol. Step (xi) is then replaced by a drying step of the resulting precipitate, the temperature ranging from about 20°C to about 60°C, preferably about 40°C.

According to the invention, the method moreover shows the complementary and/or alternative following features :

- the chosen acetic anhydride quantity ranges from 3 to 7 mols/mol of anhydroglucose, preferably about 3,2 mols/mol of anhydroglucose,
- the chosen esterification time ranges from 1 to 60 minutes, preferably about 20 to 30 minutes,
- the chosen esterification temperature ranges from 25°C to about 80 %, preferably about 40°C,
- the starting cellulose material is selected in the group comprising purified cellulose residues from co-products derived from agriculture and more particularly, from cereal bran, for example wheat and corn, but also from wood cellulose, for example pine-tree..., or from commercially-available microcrystalline cellulose of Avicel cellulose type, for example. The process according to the invention thus shows its feasibility on different cellulose sources and thus of various purities, containing notably from 60 % to 100 % cellulose,
- in the case where the cellulose originates from cereal bran, the starting cellulose material is subjected to a preliminary acidic or basic treatment for extracting non cellulose polymers ; more preferably, said preliminary treatment is performed in the presence of a reducing agent such as sodium borohydride.

The present invention also aims at a blend of hydrosoluble cellulose sulfoacetate derivatives likely to be obtained with the process according to

the invention and characterized in that said derivatives have an acetylation degree ranging preferably from 1.5 to about 2.4. The acetyl groups of the sulfoacetates probably take part in inter-chain interactions able to increase the viscosity in a very large extent.

- 5 Preferably the sulfoacetate derivatives according to the present invention have a sulphation degree ranging from about 0.2 to about 0.6, preferably about 0.3.

10 The sulfoacetate derivatives according to the invention also show the following complementary and/or alternative features and/or advantages :

- only the carbon atom which is in position 6 of the anhydroglucose cycles of said derivatives is sulphated ; thus, the sulphates increase the cellulose hydrophilic character and tend to make the derivative hydrosoluble,
- 15 - said derivatives are obtained from cellulose having a viscosimetric mean polymerization degree determined in cupric ethylene diamine at 25°C ranging from 210 to 1 590,
- the intrinsic viscosity of the blend of said derivatives, determined by extrapolation at a nil concentration of the reduced viscosity measured in water at 25°C ranges from
20 about 600 to about 1 500 ml/g and comparable to that of carboxymethylcellulose,
- said derivatives have water retention properties such that in the presence of salts, they swell up to 200 ml/g but remain insoluble,
- 25 - the blend of said derivatives is free from triacetylated derivatives which have been eliminated in the course of the process,
- said derivatives are thermally stable for 16 hours at 80°C, despite the presence of the sulphate groups,
- 30 - the blend of said derivatives may have the form of a thermoreversible and partially thixotropic gel.

Example 1 : Obtention of cellulose sulfoacetates

1.1. Starting celluloses

The different celluloses have been obtained from a wheat bran, a corn bran and a commercially-available cellulose (Avicel cellulose, sold by Fluka). In table I hereunder, two brans are described which have been subjected to various non cellulosic polymer extraction treatments (heteroxylans and lignin) through an acidic or basic process. The conditions are described hereunder.

1.1.1. Obtention of the cellulose residues

1.1.1.1. Operating mode 1

Wheat bran is suspended (50 g/l) in a sulphuric acid solution (0.5 mol/l) in the presence of a few octanol drops. The suspension is stirred for 12 hours at 110°C in an oil bath and at reflux. The residue is recovered by filtration (porosity < 15 µm) and is washed with deionized water until the wash water pH reaches 5. The cellulose residue is finally washed with ethanol (3 times, 500 ml), and then with acetone (3 times, 500 ml) and finally dried in a drying-room ventilated at 40°C for 16 hours.

1.1.1.2. Operating mode 2

The starting wheat bran or the one treated by sulphuric acid (operating mode 1) is stirred and heated in deionized water (67 g/l) until the temperature reaches 70°C. The glacial acetic acid (12 ml/l) and the sodium chlorite monohydrate (17 g/l) are then added. After 1 hour at 70°C, the same quantity of glacial acetic acid and sodium chlorite is added and the blend is stirred for 1 hour. The residue is recovered by filtration (porosity < 15 µm) and washed with deionized water until the wash water pH reaches 5. The delignified residue is then washed with ethanol (3 times, 500 ml), and then with acetone (3 times, 500 ml) and finally dried in a drying-room at 40°C for 16 hours.

1.1.1.3. Operating mode 3

Brans are suspended in a potassium hydroxide solution, 1.5 mol/l for corn bran and 2 mol/l for wheat bran. The suspension is maintained at 100°C for 2 hours with a periodic manual stirring. The residue is recovered after centrifugation (15 000 g, 30 minutes) and is washed with deionized water (3 times, 600 ml). The pH is adjusted at 6 with glacial acetic acid and the residue is washed with 95 % ethanol (3 times, 500 ml), and then with

acetone (3 times, 500 ml), and is finally dried in a drying-room ventilated at 40°C for 16 hours. The residue is then crushed and sieved (particle diameter < 0.5 mm).

1.1.1.4. Operating mode 4

- 5 The brans are suspended in a potassium hydroxide solution, 1.5 mol/l for corn bran and 2 mols/l for wheat bran, to which 10 g/l sodium borohydride are added. The suspension is maintained at 100°C for 2 hours with periodic manual stirring. The residue is recovered after centrifugation (15 000 g, 30 minutes) and is washed with deionized water (3 times, 10 600 ml). The pH is adjusted at 6 with glacial acetic acid and the residue is washed with ethanol at 95 % (3 times, 500 ml), followed by acetone (3 times, 500 ml) and is finally dried in a drying-room ventilated at 40°C for 16 hours. The residue is then crushed and sieved (particle diameter < 0.5 mm).

15 1.1.1.5. Operating mode 5

- 20 The brans are suspended (100 g/l) in a potassium hydroxide solution, 1.5 mol/l for corn bran and 2 mol/l for wheat bran, to which are added in a known way 10 ml/l of 130 volume hydrogen peroxide. The suspension is maintained at 100°C for 2 hours with a periodic manual stirring. The residue is recovered after centrifugation (15 000 g, 30 minutes) and is washed with deionized water (3 times, 600 ml). The pH is adjusted at 6 with glacial acetic acid and the residue is washed with ethanol at 95 % (3 times, 500 ml), and then with acetone (3 times, 500 ml) and is finally dried in a drying-room ventilated at 40°C for 16 hours. The residue is then 25 crushed and sieved (particle diameter < 0.5 mm).

Table I : Extraction treatments for non cellulose polymers (heteroxylans and lignin) of wheat and corn brans

Cellulose source	Sample	Operating mode	Treatment
Wheat bran	1	1+2	Sulphuric acid, then sodium chlorite
	2	2+3	Sodium chlorite, then potassium hydroxide
	3	2+4	Sodium chlorite, then potassium hydroxide + sodium borohydride
Corn bran	4	4	Potassium hydroxide + sodium borohydride
	5	5	Potassium hydroxide + hydrogen peroxide
Avicel cellulose (Fuka)	6	-	Commercial cellulose

- 5 These conditions lead to samples having features that can be very different as to the composition and the length of the cellulose chains (Table II).

10 Table II : Yield (mg/g), composition (mg/g), viscosimetric mean polymerization degree (DP_v) and crystallinity (C) of the cellulose samples

Sample	Yield	Non cellulosic oses	Cellulose	Ashes	Lignin	DP_v	C
1	217	134	581	1	132	270	Weak
2	201	282	554	26	7	940	Weak
3	208	299	587	25	6	1 150	Weak
4	224	279	603	29	7	1 250	Weak
5	157	184	729	13	8	720	Weak
6	-	Trace	974	0	0	210	Strong

- Non cellulosic oses = heteroxylans (arabinose + xylose + galactose + glucuronic acid) + mannose + non cellulosic glucose
- DP_v = viscosimetric mean polymerization degree determined in a continuous way in cupric ethylene diamine at 25°C
- 5 • C (crystallinity) = determined by X ray diffraction (selected wave length $\lambda_{CuK_{\alpha 1}} = 0.15405$).

As Fig. 1 shows, the acetic anhydride quantity added to a cellulose residue should be lower than about 2 to 7 mols per mol of anhydroglucose and, preferably, about 3.2 mols per mol of anhydroglucose. Lower acetic
10 anhydride quantities do not allow any esterification in the conditions indicated in Fig. 1 (time : 30 minutes, temperature : 40°C) and higher quantities lead to the formation of a cellulose triacetate.

Fig. 2 shows that the reaction time should be below 1 hour and preferably of about 20 to 30 minutes in the conditions indicated in Fig. 2
15 (temperature and reactive quantity). For a reaction time superior or equal to about 1 hour, the esterification produces cellulose triacetate.

Both figures illustrate the production of an esterification residue which is rich in non cellulose polymers. This residue is not obtained for high purity celluloses.

20 1.2. Obtention of cellulose sulfoacetates

1.2.1. Optimization of the obtention conditions

The cellulose sulfoacetates are obtained according to the protocol described later. Two reaction temperatures have been tested : 25°C and 40°C. At 25°C, no reaction is observed. The influence of the acetic
25 anhydride quantity and of the reaction time has been studied at 40°C (see Figs. 1 and 2).

1.2.1. Operational mode

The cellulose material, obtained as indicated hereabove, is suspended in an acetic acid solution (50 g/l), and then left under magnetic
30 stirring for 15 minutes at room temperature. After centrifugation (2 250 g, 10 minutes, 20°C), the supernatant is eliminated. This step is repeated twice.

The cellulose (50 g/l) is then dipped at room temperature into an acetic acid and sulphuric acid solution (12 g/l) and the whole is thoroughly
35 stirred for 1 minute at room temperature.

The acetic anhydride (3.2 mols per mol of anhydroglucose) is added and the reaction blend is thoroughly stirred for 1 minute, and then placed under rotating stirring at 40°C for 30 minutes.

5 The reaction is stopped by adding a 70 % acetic acid solution in order to eliminate the excess acetic anhydride and the blend is stirred for 30 minutes at room temperature.

After centrifugation (2 250 g, 10 minutes, 35°C), the supernatant is recovered and the residue is washed three times with acetic acid, followed by three times with deionized water.

10 The acetic acid and the wash waters are added to the supernatant.

Deionized water (4 volumes) is placed in a centrifugation tube and the cellulose ester solution is slowly added under magnetic stirring. The blend is placed at 4°C for 16 hours in order to precipitate the optionally generated cellulose triacetates.

15 The supernatant is recovered by centrifugation (17 500 g, 20 minutes, 4°C), and then neutralized at pH 7.5, by a slow sodium hydroxide addition at 4 mol/l.

The blend is cooled in an ice bath and the pH is continuously observed in order to avoid any saponification.

20 The resulting precipitate is then dialyzed against deionized water until the conductivity of the dialysis waters is lower than 1 μ S/cm.

1.3. Results

At 40°C, the acetic anhydride quantities may range from 3 to 7 mols per mol of anhydroglucose when the reaction time is equal to 25 30 minutes. The yields are optimal for a period of time ranging from about 20 minutes to about 30 minutes, when the acetic anhydride quantity is equal to 3.2 mols per mol of anhydroglucose.

The influence of the sulphuric acid quantity has not been tested. The sulphuric acid quantity probably influences the sulphation rate and 30 hence the water solubility. Besides, too high sulphuric acid quantities can cause a depolymerization of the cellulose and thereby affect the rheological properties of the resulting derivatives.

The esterification yield is high, but depends on the cellulose purity (Table III). It varies around 1.3 g/g for cellulose residues obtained from

cereals brans – the cellulose content of which ranges between 550 and 730 mg/g and reaches 1.7 g/g for commercial cellulose.

The acetylation degrees range from 1.8 to 2.4 and the sulphation degree is usually 0.3 (except for sample 2, where it is equal to 0.4).

5

Table III : Esterification yield (g/g), cellulose content (mg/g), acetylation (DA) and sulphation (DS) degrees, intrinsic viscosity (ml/g) and crystallinity of the cellulose sulfoacetates according to the invention as a function of the starting cellulose

10

Sample	Esterification yield	Cellulose	DA	DS	[η]	Crystallinity
1	1.3	364	2.0	0.3	nd	Nil
2	1.2	408	2.4	0.4	1 534	Nil
3	1.2	434	1.9	0.3	768	Nil
4	1.2	443	1.8	0.3	637	Nil
5	1.3	445	1.8	0.3	642	Nil
6	1.7	531	2.3	0.3	1 470	nil

η = intrinsic viscosity in water at 25°C. Flow measures in an Ubbelohde type capillar tube (diameter : 0.52) have been performed at different concentrations. The intrinsic viscosity is then determined by nil concentration extrapolation of the reduced viscosity.

15

Nd = not measured.

20

The absence of cellulose depolymerization during the esterification reaction has been shown for sample 6 (table III) : the derivative polymerization degree is therefore the same as that of the starting cellulose. This ranges from 210 to 1 250 for samples 1 to 6 (table II) and it does not seem to affect the esterification yields and the cellulose derivative properties.

25

1.4. Properties of the cellulose sulfoacetates according to the invention

The solubility in water and polar solvents is related to the presence of the sulphates which make the polymers sufficiently hydrophilic, as already mentioned.

Moreover, the acetyls confer to the derivatives of the present invention their interesting associative properties : high intrinsic viscosity depending on the acetylation degree (table III). The high intrinsic viscosity (650 - 1 500 ml/g) comparable to that of the carboxymethylcellulose implies potentially interesting thickening properties.

Example 2 : Obtention of thermoreversible gels based on the cellulose sulfoacetates of the invention

Other interesting properties conferred to the derivatives of the invention by the acetyl groups include thixotropy and gelification after thermal treatment.

The solubilization should preferably be hot performed in order to obtain a clear solution at a temperature from about 25°C to about 100°C, preferably at approximately 80°C. For a 20 mg/ml concentration and after solubilization at 80°C and slow cooling, for example a decrease of 1°C/mn to reach 20°C, a weak gel is obtained, characterized by the value of modulus G' and G'' (respectively storing and loss modulus) which are respectively 550 and 80 Pa at 1 rad/s and by applying a 5 % deformation amplitude. This gel is stronger, i.e. having higher G' and G'' module values and the divergence between the modulus is higher when the concentration is high and the temperature decrease is slow. For concentrations ranging from about 10 to about 20 mg/ml, the resulting concentration is very viscous (G' ranging from 10 and 60 Pa at 1 rad/s and G'' ranging from 0.5 and 5 Pa at 1 rad/s). For concentrations lower than about 10 mg/ml, a little viscous solution is obtained.

2.1. Properties of cellulose sulfoacetate gels

The cellulose sulfoacetate gels according to the invention are thermoreversible (no loss of the rheological properties is observed after a thermal treatment) and partially thixotropic (the gel destruction when applying a shear is not irreversible and after some rest, it tends to recover its initial state).

Thermal treatments do not cause sulphuric ester link degradation. There is therefore no sulphuric acid release which could, in the course of time, hydrolyze the polymer.

According to the present description, the expression "glacial acetic acid" should be understood as meaning acetic acid that is substantially pure at 100 %.

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CLAIMS

1. Process for directly producing a blend of hydrosoluble cellulose sulfoacetate derivatives through esterification of a cellulose material,
5 comprising the steps of :

(i) suspending the cellulose material in a glacial acetic acid solution and eliminating the excess acetic acid,

(ii) suspending the cellulose material swollen of acetic acid in a sulphuric acid solution in the glacial acetic acid, and

10 (iii) reacting the cellulose material by adding the acetic anhydride, characterized in that :

- the chosen acetic anhydride quantity ranges from 3 to 7 mols/mol of anhydroglucose,
- the esterification time ranges from 1 to 60 mn, and
- 15 - the esterification temperature ranges from 25 to 80°C.

2. Process according to claim 1, characterized in that it comprises a step (iv) during which the step (iii) reaction is stopped by adding an acetic acid aqueous solution.

20 3. Process according to claim 2, characterized in that it comprises the steps of :

(v) optionally centrifuging the blend of the above-mentioned step (iv),

25 (vi) washing and eliminating the optionally obtained residue,

(vii) adding water in order to precipitate the optionally generated cellulose triacetates,

(viii) centrifuging and eliminating the residue,

(ix) neutralizing the supernatant by optional cooling,

30 (x) dialyzing the resulting precipitate, and

(xi) freeze-drying the solution.

4. Process according to claim 3, characterized in that at step (vi), the residue is washed three times with acetic acid, and then three times with
35 deionized water.

5. Process according to claim 3 or 4, characterized in that, at the step (vii), the blend is put at a temperature of about 4°C for about 16 hours.

5 6. Process according to anyone of claims 3 to 5, characterized in that the step (ix), is carried out by a slow addition of a sodium hydroxide solution until a pH of about 7.5 is reached.

10 7. Process according to anyone of claims 3 to 6, characterized in that at the step (ix) the blend is cooled in an ice bath and the pH is continuously followed so that the pH does not exceed 10.

8. Process according to claim 8, characterized in that the pH does not exceed 7.5.

15 9. Process according to anyone of the preceding claims, characterized in that the chosen acetic anhydride quantity is 3.2 mols/mol of anhydroglucose.

20 10. Process according to anyone of the preceding claims, characterized in that the chosen esterification time ranges from 20 to 30 mn.

11. Process according to anyone of the preceding claims, characterized in that the chosen esterification temperature is 40°C.

25 12. Process according to anyone of the preceding claims, characterized in that the starting cellulose material is selected in the group comprising cellulose residues purified from co-products derived from agriculture and, more particularly, from cereal bran, for example wheat and corn, but also from wood cellulose, for example, pine-tree, or
30 microcrystalline cellulose.

13. Blend of hydrosoluble cellulose sulfoacetate derivatives adapted to be obtained using a process according to anyone of the preceding claims, characterized in that said derivatives have an acetylation degree
35 ranging from 1.5 to 2.4.

14. Derivative blend according to the preceding claim, characterized in that said derivatives have a sulphation degree ranging from 0.2 to 0.6.

5 15. Derivative blend according to claim 14, characterized in that said derivatives have a sulphation degree of 0.3.

10 16. Derivative blend according to anyone of claims 13 to 15, characterized in that only the carbon atom which is in position 6 of the anhydroglucose cycles of said derivatives is sulphated.

15 17. Derivative blend according to anyone of claims 13 to 16, characterized in that said derivatives have a viscosimetric mean polymerization degree determined in cupric ethylene diamine at 25°C ranging from 210 to 1 590.

20 18. Derivative blend according to anyone of claims 15 to 17, characterized in that said blend intrinsic viscosity, determined by extrapolation at nil concentration of the reduced viscosity measured in water at 25°C ranges from 600 to 1 500 ml/g.

25 19. Blend according to anyone of claims 13 to 18, characterized in that said derivatives have such water retention properties that in the presence of salts, they swell up to 200 ml/g while remaining insoluble.

20. Blend according to anyone of claims 13 to 19, characterized in that it is free from triacetylated derivatives.

30 21. Blend according to anyone of claims 13 to 20, characterized in that said derivatives are thermally stable for 16 hours at 80°C.

22. Blend according to anyone of claims 13 to 21, characterized in that it has the form of a thermoreversible and partially thixotropic gel.

ABSTRACT OF THE DISCLOSURE

A method for directly producing a mixture of cellulose sulfoacetate derivatives by esterification of cellulosic material, characterized in that it comprises the following steps i) the cellulosic material is suspended in a glacial acetic acid solution and the excess acetic acid is eliminated ii) the cellulosic acid that is swollen with acetic acid is suspended in a sulfuric acid solution in glacial acetic acid and iii) the cellulose material is made to react by adding acetic anhydride.

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PRODUCING CELLULOSE SULFOACETATE DERIVATIVES AND PRODUCTS AND MIXTURES THEREOF

the specification of which: *(check one)*

REGULAR OR DESIGN APPLICATION

☐ is attached hereto.

☒ was filed on ~~the 30th of July 1999~~ application Serial No. 09/890,348
and was amended on (if applicable).

PCT FILED APPLICATION ENTERING NATIONAL STAGE

☒ was described and claimed in International application No.
PCT/FR00/00205 filed on 28 January 2000 and as amended on
(if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

PRIORITY CLAIM

I hereby claim foreign priority benefits under 35 USC 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

Country	Application Number	Date of Filing (day, month, year)	Priority Claimed
France	99 01049	29 January 1999	yes

(Complete this part only if this is a continuing application.)

I hereby claim the benefit under 35 USC 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 USC 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status—patented, pending, abandoned)

POWER OF ATTORNEY

The undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from Cabinet Harle & Phelip as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

As a named inventor, I hereby appoint the registered patent attorneys represented by Customer No. 000466 to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Robert J. PATCH, Reg. No. 17,355, Andrew J. PATCH, Reg. No. 32,925, Robert F. HARGEST, Reg. No. 25,590, Benoît CASTEL, Reg. No. 35,041, Eric JENSEN, Reg. No. 37,855, Thomas W. PERKINS, Reg. No. 33,027, and Roland E. LONG, Jr., Reg. No. 41,949

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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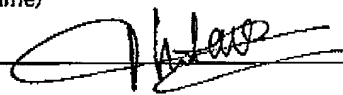
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